이학석사 학위논문

Synthesis and Solution Self-Assembly of Hetero-Arm Polymers Based on POSS

포스를 기반으로 한 블록 공중합체의 합성 및 용액 자기조립 연구

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孙雨霖의 이학석사 학위논문을 인준함

2019 년 08 월

위 원 장 손 병 혁 (인)

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Abstract

Synthesis and Solution Self-Assembly of Hetero-Arm Polymers Based on POSS

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Seoul National University

Self-assembly of block copolymers to give cubosome structures is an emerging phenomenon, which could provide new polymeric mesoporous materials with a three-dimensionally organized internal maze of large water channels. The architecture of block copolymers critically influences the self-assembled structure. Here we designed and synthesized a series of hetero-arm block copolymers PEG_7-POSS-*n*PS (n = 1, 2) whose arms are precisely arranged on a T8 polyhedral oligomeric silsequioxane (POSS), an inorganic cage that can be asymmetrically functionalized to host structural modules to provide a variety of spatial and chemical environments. The synthesis begins with the POSS compound with one hydroxylethyl and seven vinyl pendant groups. Seven polyethylene glycol (PEG) arms are introduced to the vinyls through thiol-ene reaction, then the hydroxyl group is converted to alkyne for subsequent "grafting" of polystyrene (PS) arm onto POSS. By adjusting the molecular weight of polystyrene or composition of the solvent, a

series of block copolymers PEG_7-POSS-*n*PS self-assemble into the desired structures, which range from vesicles to polymer sponges, polymer cubosomes and aggregated colloids. The resulting block copolymers might provide diversities of chemical structures of block copolymers in the creation of complex nanostructures by self-assembly.

Keyword: Hetero-arm Polymer, T8 polyhedral oligomeric silsequioxane (POSS), Poly(ethylene glycol), Polystyrene, Solution self-assembly, Nanostructure
Student Number: 2017-26141

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1. Introduction

In the past two decades, new devices such as cell phone, micro-processor and new medicines have altered the way people live. Development of new materials have revolutionized the industry and led to a proliferation of new products. Macroscopic materials are composed by microscopic atoms and molecules, macroscopic properties of materials are related to these chemical structures. To prepare new materials with desired functions, it is important to realize the relationship between properties and chemical structures and to design proper structures. Materials in nanoscale show many special properties that macroscopic materials do not have, such as surface effect and quantum dimension effect, these properties provide better conductivity, magnetic permeability and chemical reactivity[1]. However, these microscopic properties are arduous to transfer into the macroscopic level directly. Therefore, how to amplify the micro-properties into macro level has become an attractive research topic[2].

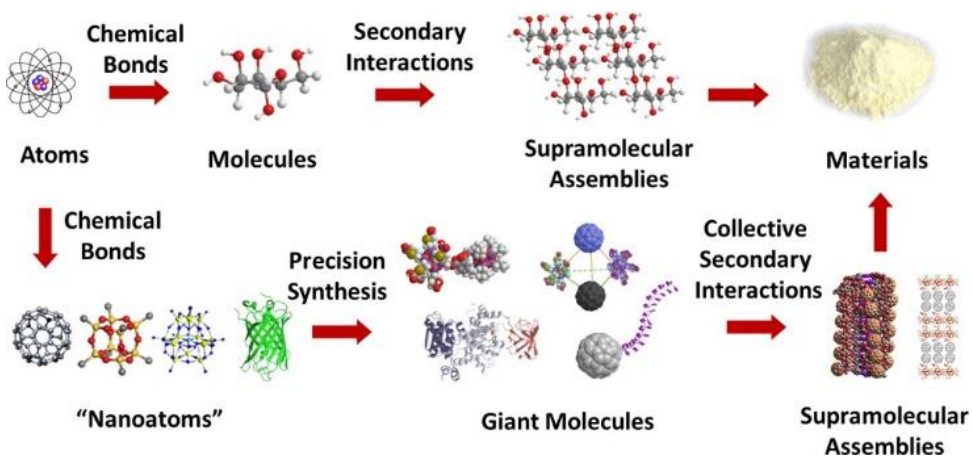


Figure 1.1. Two ways to obtain materials: from atoms to molecules and from nano-atoms to giant molecules

Hierarchical structures across different length scale are thought to be an effective amplifier in the procedure for amplifying the micro-properties of materials into macro level, which have a wide variety of applications in the fields of organic electronics, solid-state electrolytes, and nanotemplating[3, 4]. Hierarchically ordered structures are commonly prepared by self-assembly of traditional molecules through noncovalent interactions. The self-assembled structure can be adjusted by modifying the chemical structure of molecules because the dynamics to from hierarchical structures is minimization of free energy[5, 6].

Amphiphilic block copolymers (BCPs) composed of hydrophilic and hydrophobic blocks self-assemble in solution to form micelles and vesicles in an analogous fashion to lipids. In addition to the morphological diversity, recent efforts have been placed on polymer micelles and vesicles with well-defined internal order. The inverse cubic mesophases of lipids and their colloidal forms (cubosomes) possess internal networks of water channels arranged in crystalline order, with provide a unique nanospace for membrane-protein crystallization and guest encapsulation. Recently, many studies were reported for the formation of cubosomes by direct self-assembly of block copolymers in dilute solution, which provide new methods for the preparations of polymeric mesoporous materials with a three-dimensionally organized internal maze of large water channels[7-10]. Eisenberg and coworkers[11-13] reported that the self-assembly of a diblock copolymer, poly(acrylic acid)-*b*-polystyrene (PAA-*b*-PS) having highly asymmetric architecture, self-assembled in solution into nanoparticles having internal hexagonal hollow hoops. Holder and Sommerdijk[14-16] reported the formation of polymer cubosomes, analogues to colloidally stabilized nanoparticles of lipid cubic mesophases (cubosomes), via solution self-assembly from amphiphilic BCPs having hydrophobic blocks of

bottlebrush-like architectures.

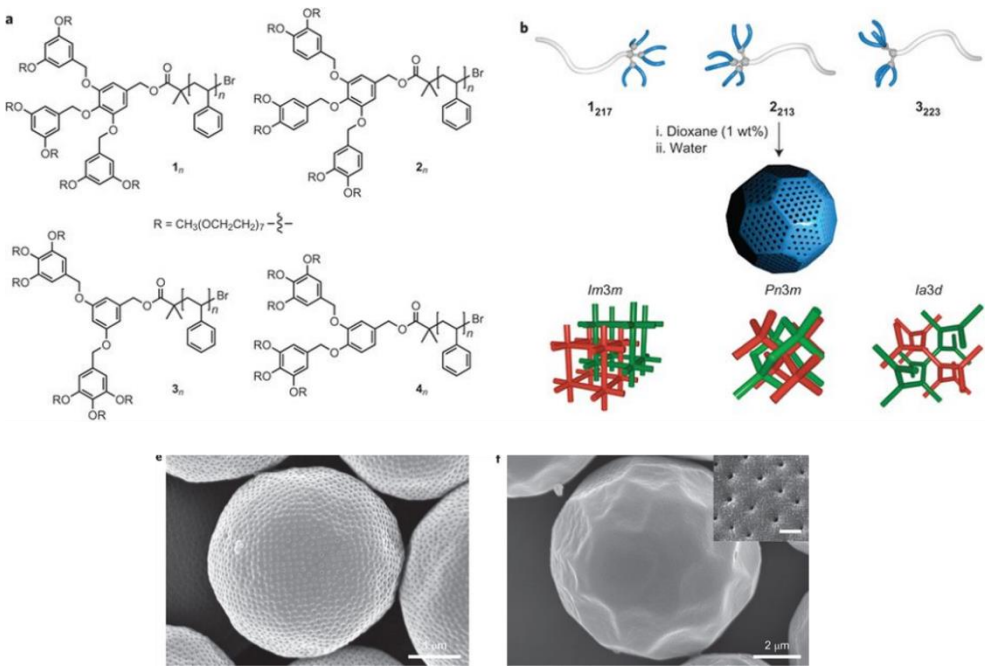


Figure 1.2. Chemical structures and schematic diagrams of dendritic–linear block copolymers and their self-assembly. a, Chemical structures of block copolymers 1n and 2n constructed from the two isomers of benzyl ether dendrons that possess peripheral PEG chains at the 3,5-positions (1n) and 3,4-positions (2n) of the outer phenyl groups, and 3n and 4n built from dendritic blocks that consist of two peripheral 3,4,5-PEG-benzyl ether units at the 3,5 (3n) and 3,4 (4n) positions of the central benzyl unit. The subscript n denotes the DP of the PS block. b, A schematic representation of the self-assembly of dendritic–linear block copolymers into polymer cubosomes in dilute aqueous solution. The lattice diagrams at the bottom show bicontinuous cubic internal structures of the polymer cubosomes (Im3m, Pn3m and Ia3d) investigated in this study. For clarity, the bilayers that surround the water channels are omitted. The green- and red-coloured regions indicate two non-intersecting networks of water channels within the bicontinuous structures. e and f, SEM images of polymer cubosomes

Giant molecules, referring to molecular nanoparticles (MNPs) of nano-scale sizes and fixed shapes, could be utilized as perfect building blocks to prepare various molecules, which provide new avenues for controlled hierarchical assembly. Polyhedral Oligomeric Silsesquioxane (POSS) is the smallest silica nanoparticle having an in organic core diameter of about 1.0 nm[17, 18], and its vertex could be functionalized to prepare hybrid molecules[19, 20]. The T8 POSS has a cubic framework possessing a high O_h symmetry (POSS refers to T8 POSS hereinafter unless otherwise stated). Many studies have been conducted to the POSS derivatives, short alkyl chains substituted POSS have good ability of crystallization at room temperature[21-23], and the crystal structure can be adjusted by changing the substantial groups. As an inorganic nanoparticle, POSS can be also introduced to polymer chains to enhance the chemical and physical properties such as modulus, glass transition temperature and thermal stability[24-26].

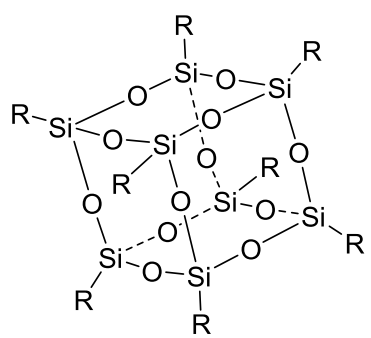


Figure 1.3. Chemical structure of alkyl chains substituted polyhedral oligomeric silsesquioxane (POSS)

With the development of synthetic technologies, it is possible to control the locations of multiple tethering sites on a molecular nanoparticle to prepare star polymers with desired chemical structures. Due to its well-defined chemical structure, POSS has

also been used as the proper building block to construct well-defined polymers and block copolymers[27-32]. Cheng[33] and coworks constructed nanosized giant tetrahedra by placing different polyhedral oligomeric silsesquioxane (POSS) molecular nanoparticles at the vertices of a rigid tetrahedral framework, and illustrated that designed symmetry breaking of these giant tetrahedral introduced precise positional interactions and results in diverse selectively assembled, highly ordered supramolecular lattices.

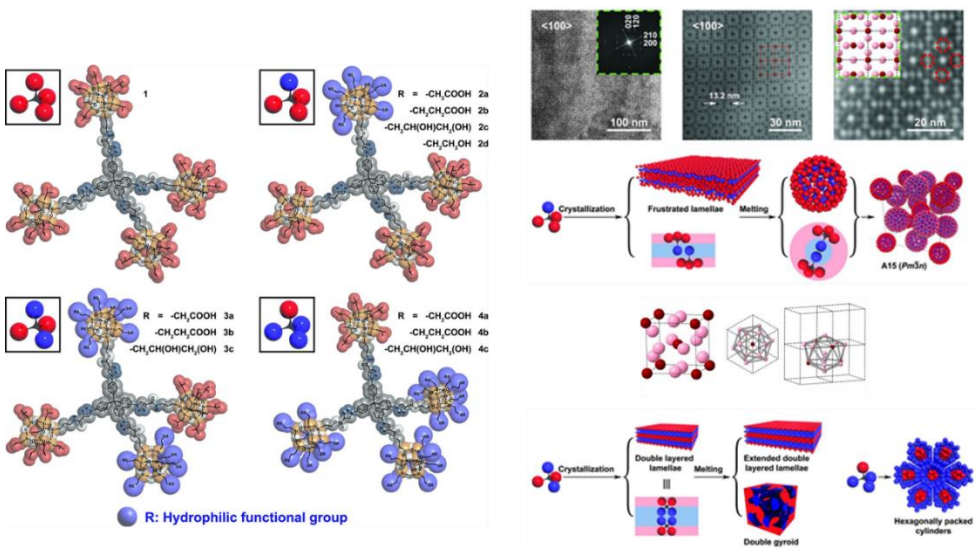


Figure 1.4. Chemical structures and molecular models (shown in shadow) of the four categories of giant tetrahedral and selectively assembled structures of 2a, 3 and 4.

Zhang[34] and coworkers precisely arranged hetero polymer and small molecular chains onto POSS, building a series of giant surfactants and star polymers, these regioisomers gave obviously different phase behaviors in bulk. These two studies both indicate that persistent molecular geometry with balanced enthalpy and entropy plays an important role in in creating thermodynamically stable supramolecular lattices with properties distinct from those of other self-assembling soft materials.

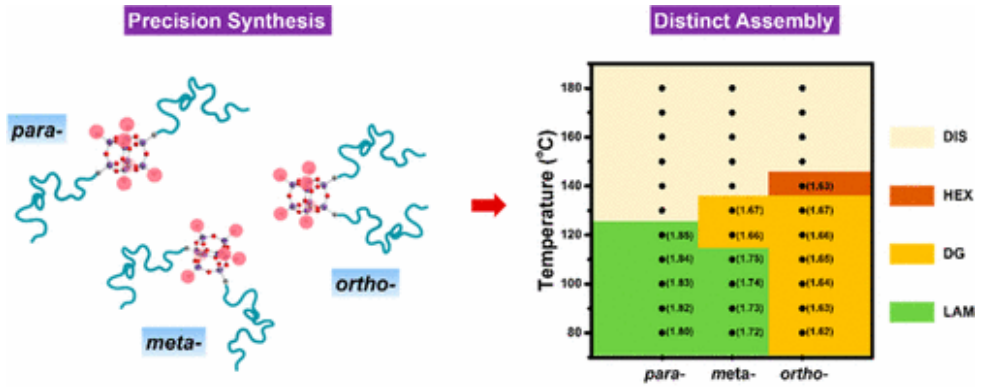


Figure 1.5. Illustration of double-chain giant surfactant regioisomers with two PS chains (cyan line) and hydroxyl-functionalized POSS head (molecular model with pink side groups) and phase diagram of p-DPOSS-2PS9 (left,), m-DPOSS-2PS9 (middle), and o-DPOSS-2PS9 (right) with respect to temperature.

The molecular packing parameter theory describes the relationship between the chemical structure of an amphiphile and the morphology of its assembled structure. Recently KT Kim[9] and coworkers reported the self-assembly of amphiphilic dendritic-linear block poly(ethylene glycol)-*b*-polystyrene (PEG-*b*-PS) into polymer cubosomes in aqueous solution, and the presence of precisely defined bulky dendritic blocks drives the block copolymers to form spontaneously highly curved bilayers in aqueous solution. Three inverse bicontinuous cubic phases (primitive cubic, double diamond and gyroid) were identified from the polymer cubosomes of our dendritic–linear block copolymers depending on the architecture of the dendritic scaffold in the hydrophilic block, suggesting that the presence of an accurately architecture in the hydrophilic block is the key structural element of the solution self-assembly of amphiphilic block copolymers into inverse bicontinuous mesophases.

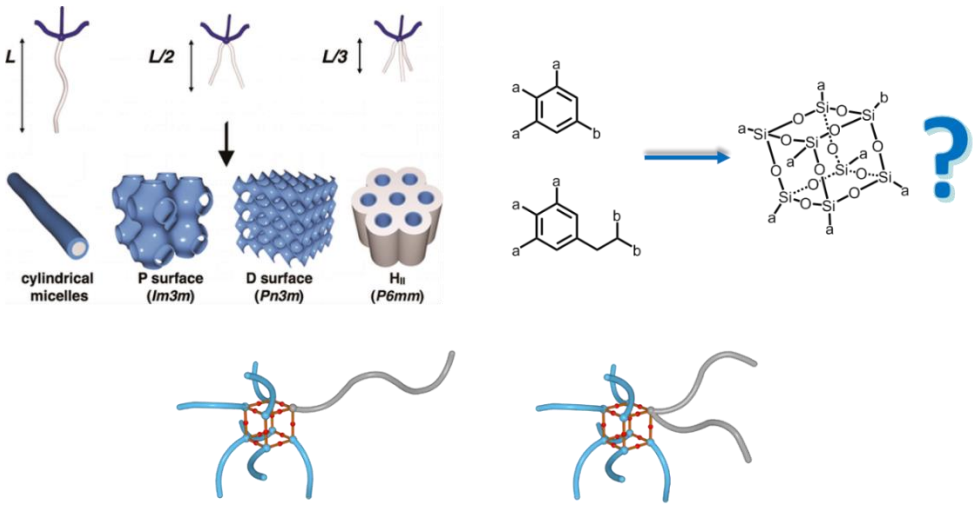


Figure 1.6. Design of hetero-arm polymers having a polyhedral oligomeric silsesquioxane (POSS) core[35]

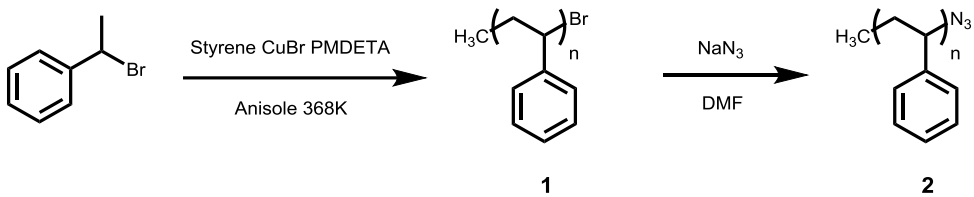
Early we have demonstrated the approaches to preferentially prepare hierarchical ordered structures by self-assembling amphiphilic BCPs in solution and shown that adjusting the chemical structures of BCPs not only influences the packing parameter (P) of BCPs but also dictates the crystalline lattice of the resulting inversed bicontinuous cubic mesophases. However, it remains nontrivial to prepare amphiphilic BCPs with unconventionally molecular geometry and study their morphologies. Thus, in this work we tend to utilize POSS instead of benzene as a linker to build a series of hetero-arm BCPs having unconventionally molecular geometry. By precisely placing polymeric chains onto polyhedral oligomeric silsesquioxane (POSS) molecular nanoparcitle to build a completely new star polymer, we expect that new assembled structures can be formed. The inorganic silicon-oxygen backbones of POSS can increase the etching contrast of the materials, and provide bulkier polymeric building blocks. Here the polyethylene glycol and polystyrene are respectively chosen as hydrophilic and hydrophobic blocks and are

precisely arranged on a POSS by sequential click-reactions. Then the solution self-assembly is achieved to study these morphologies. Finally, we illustrate the conditions under which hierarchical ordered structures can be obtained, describe the influence of rigid POSS framework in self-assembly, and find that star BCPs having a POSS core exhibit a crystalline order having absolute primitive cubic structure.

2. Results and Discussion

Design and Synthesis of Hetero-Arm Block Copolymers with a Cubic POSS Core

Synthesis of Hydrophobic Blocks



Scheme 2.1. Synthesis of azido-functionalized polystyrene (**2**)

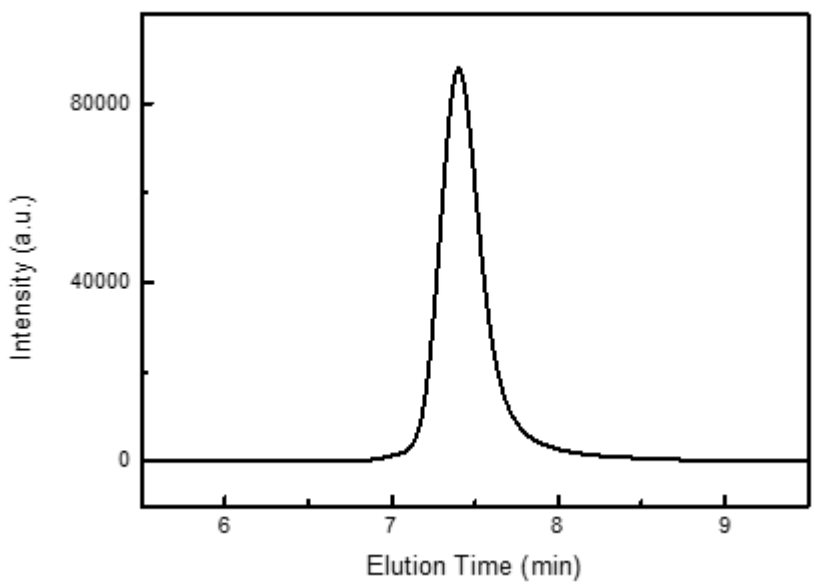


Figure 2.1. GPC spectrum of azido-functionalized polystyrene (M_n: 26.5 kg·mol^{-1}, PDI: 1.08)

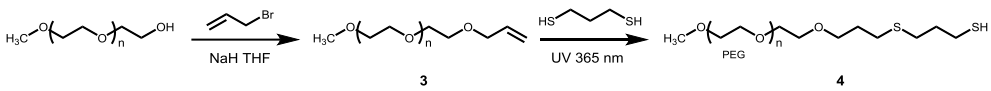
The brominated polystyrene was synthesized by atom transfer radical polymerization (ATRP) initiated by phenylethyl bromide, CuBr was used as a catalyst and PMDETA was used as a ligand. The degree of polymerization was monitored by gel permeation chromatography (GPC) and the reaction was quenched by CH_2Cl_2. After purification, brominated polystyrene and NaN_3 were dissolved in DMF and the mixture was stirred at room temperature, then the brominated polystyrene was converted to azido-functionalized polystyrene and the product was isolated by precipitating in methanol.

Table 2.1. Characterization of Azido-Functionalized Polystyrene

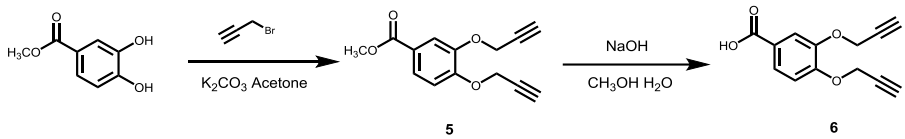
Entry	Sample	M_n (kg mol^{-1})[a]	$Đ$[a]	DP_n (PS)[b]
PS 1	PS_{86}	9.13	1.09	86
PS 2	PS_{134}	13.8	1.06	134
PS 3	PS_{211}	22.4	1.06	211
PS 4	PS_{259}	26.5	1.08	259
PS 5	PS_{317}	32.5	1.10	317
PS 6	PS_{442}	45.5	1.11	442
PS 7	PS_{509}	53.2	1.16	509

[a] The number-average molecular weight and molecular weight distribution determined by GPC (THF, 35, 0.3 mL min^{-1} flow rate) using PS standards. [b] The number-average degree of polymerization (DP_n) of the PS block determined by GPC.

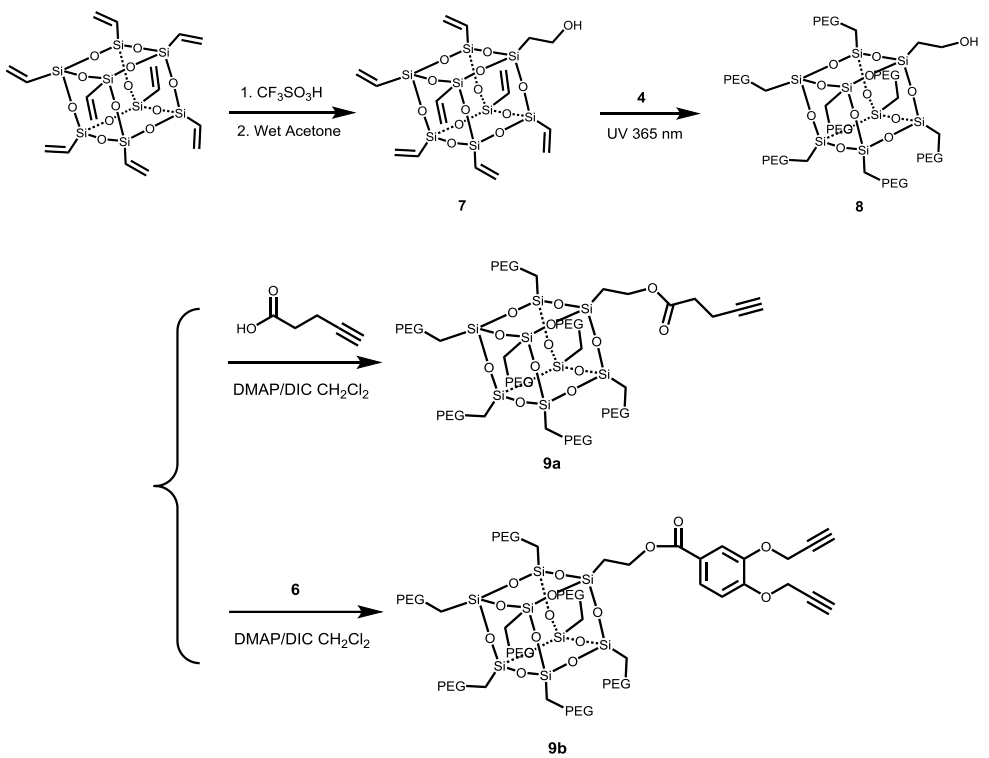
Synthesis of Hydrophilic Domains



Scheme 2.2. Synthesis of thiol terminated polyethylene glycol (**4**)



Scheme 2.3. Synthesis of 3,4-dipropargyloxybenzoic acid (**6**)



Scheme 2.4. Synthesis of PEG350$_7$-3-hydroxylpropyl-POSS (**8**), PEG350$_7$-3-(4'-pentyloxy)-propyl-POSS (**9a**) and PEG350$_7$-3-(3',4'-dipropargyloxybenzoyloxy)-

propyl-POSS (**10a**)

The branched hydrophilic modules, PEG350$_7$-POSS containing alkyne groups, were prepared from the octavinyl-POSS through hydrolysis, thiol-ene chemistry and esterification. The commercially available PEG350 was converted to PEG methyl ether thiol in 2 steps, Octavinyl-POSS is a commercially available, very useful POSS derivative, the 3-hydroxylpropylheptavinyl-POSS was first obtained by hydrolysis from the octavinyl-POSS upon the addition of triflic acid across double bonds and subsequent hydrolysis, and then seven polyethylene glycol (PEG) arms were introduced to seven vinyl groups through the thiol-ene reaction.

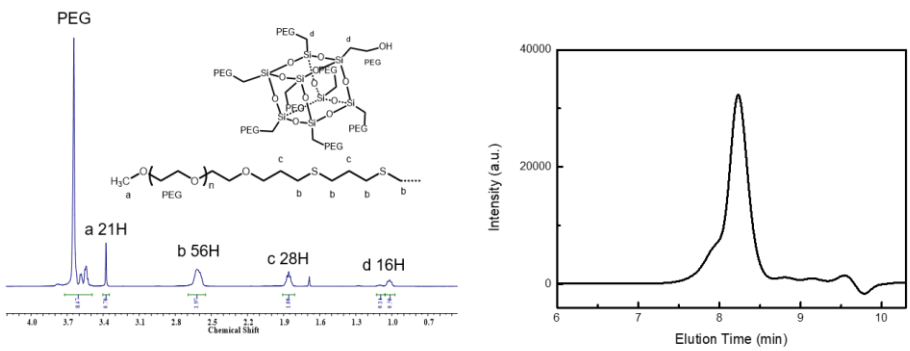


Figure 2.2. Characterization of PEG350$_7$-POSS domain

Carboxylic acids with both one or two alkyne groups were connected to the prepared hydroxyl group which was converted to alkynes for the synthesis of branched-linear hetero-arm block copolymers.

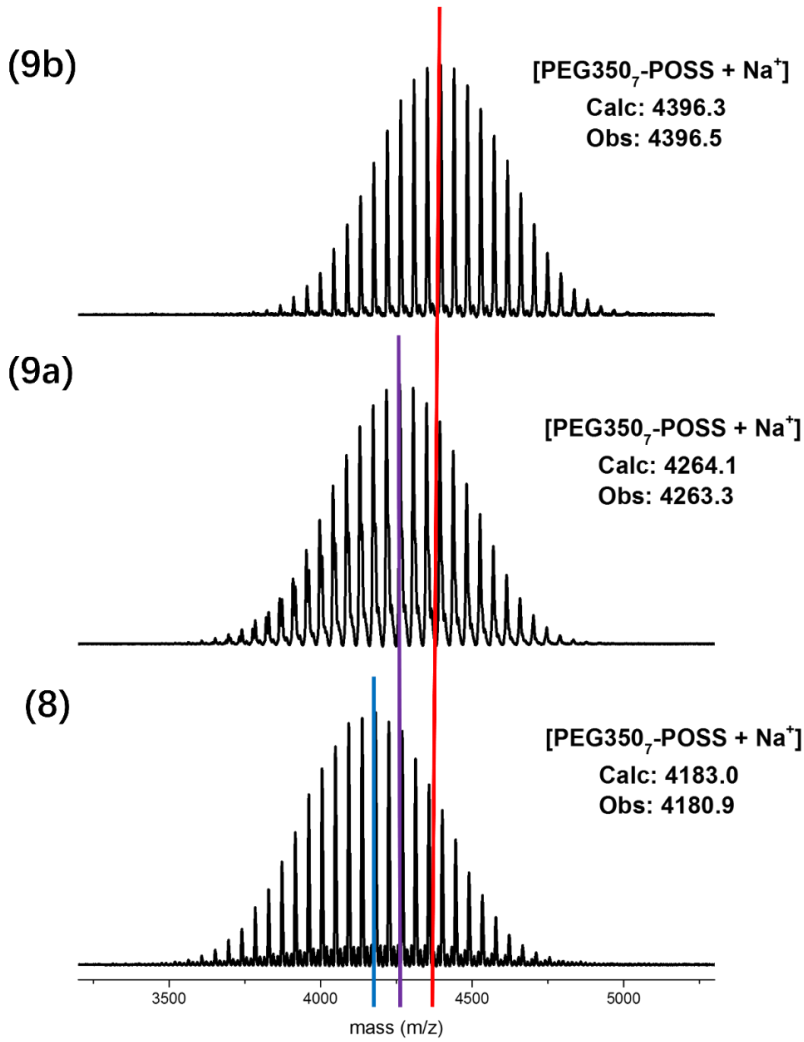
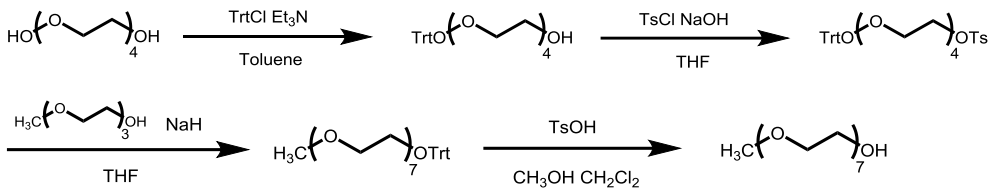


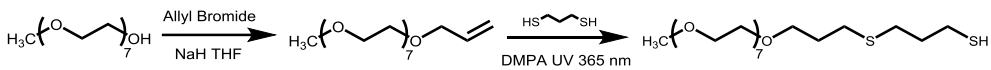
Figure 2.3. MALDI-TOF MS spectrum of PEG350$_7$-3-hydroxylpropyl-POSS (**8**), PEG350$_7$-3-(4'-pentyloxy)-propyl-POSS (**9a**) and PEG350$_7$-3-(3',4'-dipropargyloxybenzoyloxy)-propyl-POSS (**10a**)

Synthesis of Discrete Hydrophilic Domains

The discrete PEG-POSS domain was synthesized by the scheme shown as below.



Scheme 2.5. Synthesis of discrete PEG-7 mer.



Scheme 2.6. Synthesis of thiol terminated PEG-7 mer.

The discrete hydrophilic modules, $(PEG\text{-}7mer)_7$-POSS alcohol was prepared from the octavinyl-POSS through hydrolysis and thiol-ene chemistry.

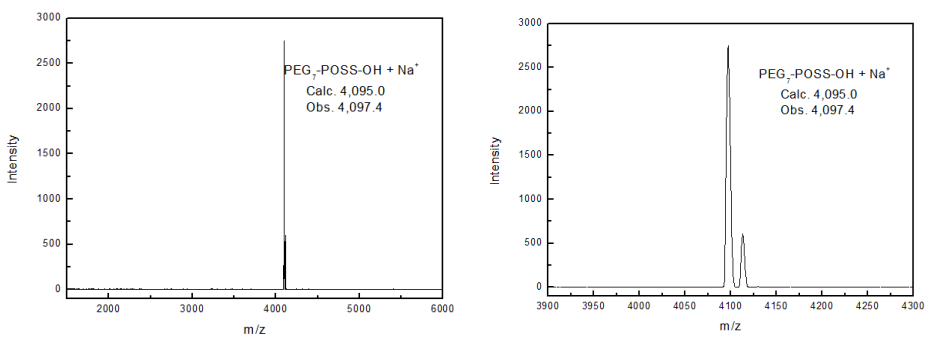
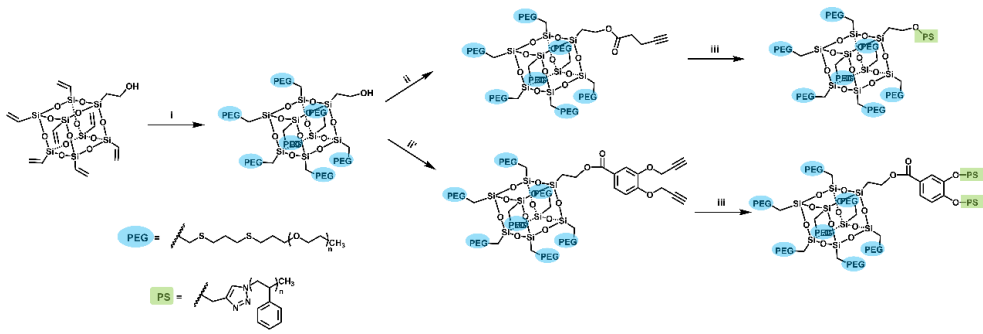


Figure 2.4. MALDI-TOF MS spectrum of hepta-PEG_7-3-hydroxylpropyl-POSS

Synthesis of Hetero-Arm Block Copolymers

The prepared hydrophobic domain and hydrophilic domain were linked by CuAAC click reaction to form block copolymers, PEG350$_7$-POSS-PS$_n$ and branched-branched block copolymers, PEG350$_7$-POSS-(PS$_n$)$_2$, with different molecular weights of PS arms at a fixed molecular weight of the PEG domain. These hydrophilic modules were characterized by GPC, ^{1}H NMR, MALDI-TOF-MS. As hydrophobic modules, azido terminated polystyrenes (PS-N$_3$) were prepared through the atom-transfer radical polymerization (ATRP) of styrene using the 1-bromoethylbenzene as an initiator, followed by the end-group conversion with NaN$_3$ in DMF. The precursors and products were purified by using suitable methods including precipitation, recrystallization and column chromatography.

Scheme 2.7. Synthesis of hetero-arm block copolymers



Regents and conditions: (i) PEG-SH, DMPA, THF, 3 h, 71 %; (ii) carboxylic acid, DMAP, DIC, THF, 24 h, ~77%; (iii) PS-N$_3$, CuSO$_4$·5H$_2$O, Na ascorbate, DMF, ~23 %.

The thin layer chromatography was used to confirm that all homo polystyrenes have been cleaned out from the block copolymers. GPC was adopted to measure the molecular weights of a series of hetero-arm block copolymers PEG350$_7$-POSS-PS and PEG350$_7$-POSS-PS$_2$, and the ratios of hydrophilic parts and hydrophobic parts

were studied by ^{1}H NMR.

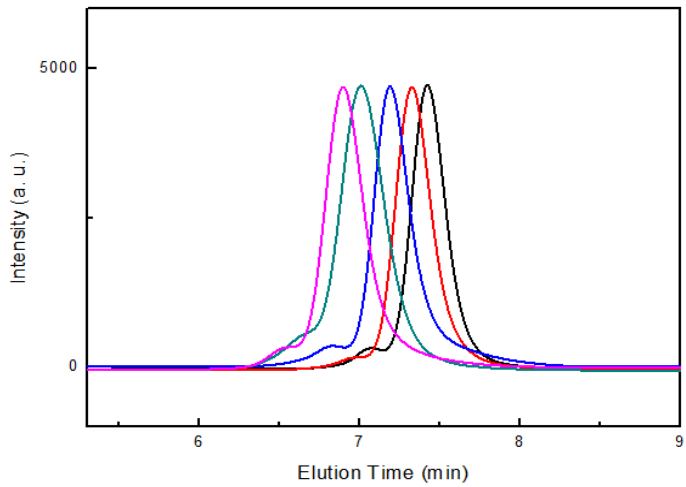


Figure 2.5. GPC results of block copolymers $PEG350_7$-PEG-PS

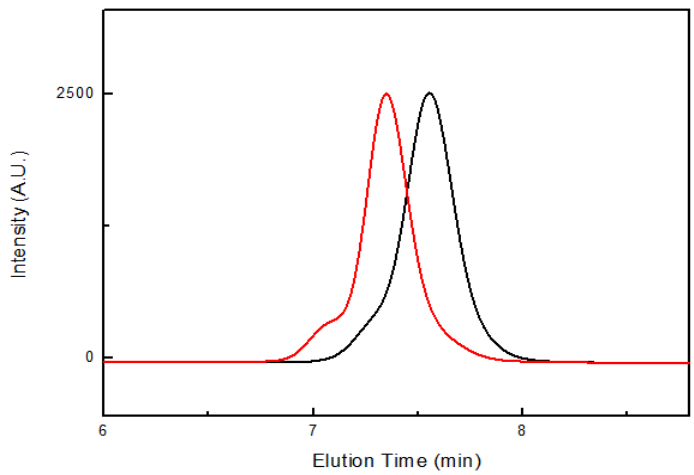


Figure 2.6. GPC results of block copolymers $PEG350_7$-PEG-PS_2

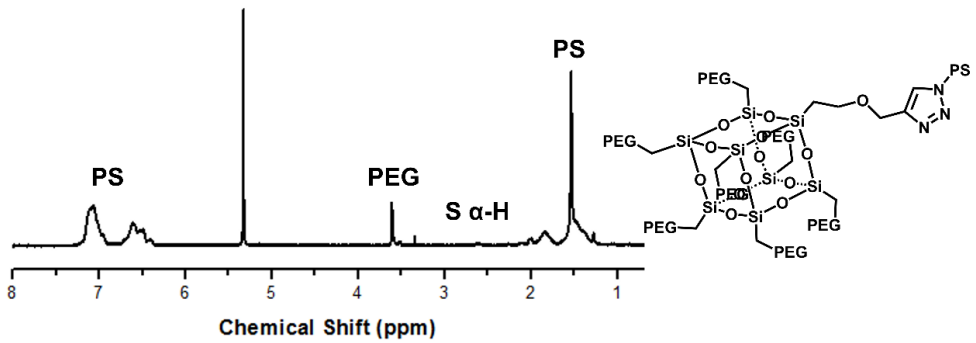


Figure 2.7. ^{1}H NMR result of block copolymer PEG350$_7$-POSS-(PS$_{442}$)

Self-Assembly of Hetero-Arm Block Copolymers into Hierarchical Ordered Structures

With the above preparation, we then investigated the solution self-assembly of a series of hetero-arm block copolymers PEG350$_7$-POSS-PS$_n$: PEG350$_7$-POSS-(PS$_{211}$), PEG350$_7$-POSS-(PS$_{259}$), PEG350$_7$-POSS-(PS$_{317}$), PEG350$_7$-POSS-(PS$_{442}$) and PEG350$_7$-POSS-(PS$_{509}$), PEG350$_7$-POSS-(PS$_n$)$_2$: PEG350$_7$-POSS-(PS$_{86}$)$_2$, PEG350$_7$-POSS-(PS$_{134}$)$_2$ and PEG350$_7$-POSS-(PS$_{240}$)$_2$. These hetero-arm block copolymers were allowed to self-assemble from a series of mixed solvents (2.00 mL, 0.25 wt%) of acetone and dioxane by adding an equal volume of water at a controlled rate (0.50 mL/h). All hetero-arm block copolymers were self-assembled under the identical condition for comparison purpose.

Table 2.2. Molecular characterizations of hetero-arm block copolymers.

Sample	M_n(PS-N_3)	PDI(PS-N_3)	M_n	PDI
PEG350$_7$-POSS-(PS$_{211}$)	22.4	1.06	27.7	1.04
PEG350$_7$-POSS-(PS$_{259}$)	26.5	1.08	31.1	1.08
PEG350$_7$-POSS-(PS$_{317}$)	32.5	1.10	37.1	1.14
PEG350$_7$-POSS-(PS$_{442}$)	45.5	1.11	53.2	1.12
PEG350$_7$-POSS-(PS$_{509}$)	53.2	1.16	61.1	1.17
PEG350$_7$-POSS-(PS$_{86}$)$_2$	9.13	1.09	21.1	1.07
PEG350$_7$-POSS-(PS$_{134}$)$_2$	13.8	1.06	2.97	1.07

We first examined the morphologies of the self-assembled structures of PEG350$_7$-POSS-PS$_n$, which has the PS block of different molecular weights in the linear hydrophobic block using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In the TEM images of dried aqueous suspension, we observed that polymer cubosomes consisting of inverse bicontinuous cubic structure of the bilayer of PEG350$_7$-POSS-(PS$_{317}$) (f_{PEG} = 7.4 %). The polymer cubosomes of PEG350$_7$-POSS-(PS$_{317}$) was obtained through its self-assembly from absolute acetone. The IBC structures was further studied by SEM and synchrotron SAXS. SEM images demonstrated the *P* minimal surface structure, in synchrotron SAXS results from the dried polymer cubosomes of PEG350$_7$-POSS-(PS$_{317}$), the diffraction peaks could also be assigned to a *P* minimal surface structure (*Im3m* symmetry). By adjusting the composition of solvent, we also observed polymer cubosomes of other samples with smaller f_{PEG} values. PEG350$_7$-POSS-(PS$_{442}$) self-assembled into polymer cubosomes from a mixed solvent of acetone/dioxane (v:v=90/10), the above results were also confirmed by SEM and synchrotron SAXS, SEM images gave *P* minimal structures (*Im3m*).

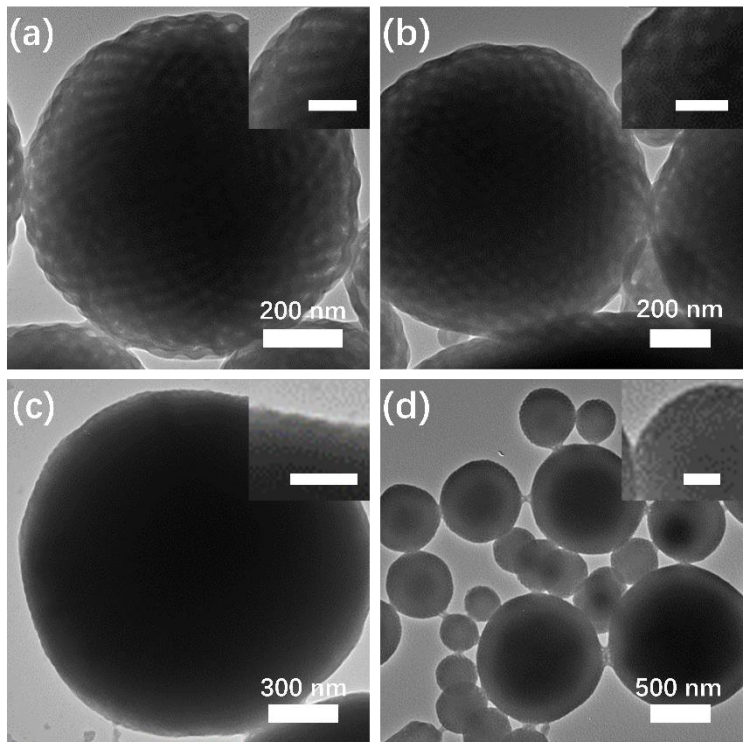


Figure 2.8. (a) TEM image showing the morphologies of PEG350$_7$-POSS-(PS$_{317}$) self-assembled in acetone; (b) TEM image showing the morphologies of PEG$_7$-POSS-(PS$_{442}$) self-assembled in acetone/dioxane (v:v=90/10); (c-d) TEM images showing the morphologies of PEG$_7$-POSS-(PS$_{86}$)$_2$ self-assembled in (c) acetone and (d) acetone/dioxane (v:v=90/10).

The branched-branched block copolymers, PEG350$_7$-POSS-(PS$_n$)$_2$ having branched hydrophobic blocks exhibited the IBC structures at considerably higher f_{PEG} values. Three samples were prepared and allowed to sample a series of acetone/dioxane solvents. Polymer cubosomes of PEG350$_7$-POSS-(PS$_{86}$)$_2$ (f_{PEG} = 13.6 %) were obtained through the solution self-assembly from mixed solvent of acetone/dioxane (v:v=100-n/n) with n ranging from 0 to 10. To further study the polymer cubosomes and determine these inner structures, SEM and synchrotron SAXS were carried out and similar results were obtained. The polymer cubosomes self-assembled from the

acetone/dioxane (v:v=95/5) had *P* minimal structures (*Im3m*).

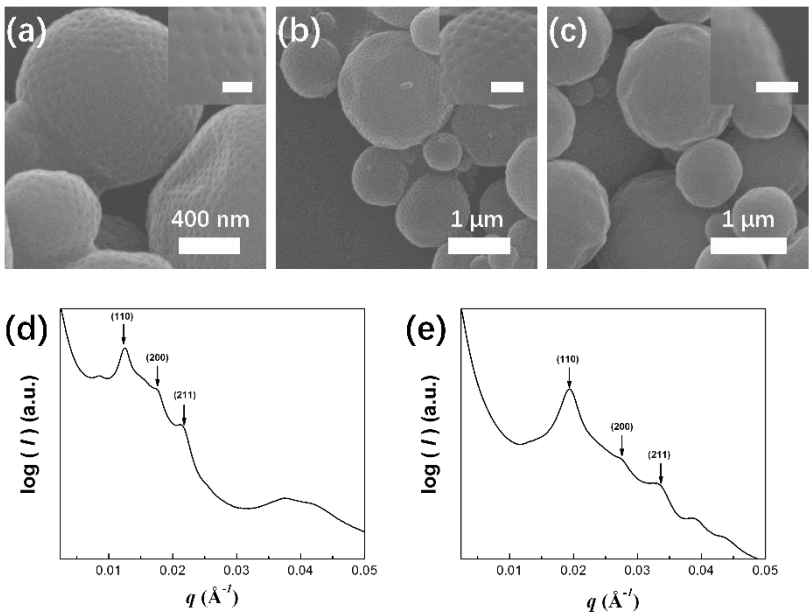


Figure 2.9. (a-c) SEM images showing the polymer cubosomes of (a) PEG_7-POSS-(PS_{317}), (b) PEG_7-POSS-(PS_{442}) and (c) PEG_7-POSS-$(PS_{86})_2$; (d, e) SAXS results obtained from dried polymer cubosomes of (d) PEG_7-POSS-(PS_{317}) and (e) PEG_7-POSS--$(PS_{86})_2$ indicating *Im3m* symmetry.

Effect of the POSS cage on the morphology of hetero-arm block copolymer

The morphology of the self-assembled structure is strongly influenced by the chemical structure of a block copolymer. According to the packing parameter theory, we know that with a fixed hydrophilic domain, the branched-linear block copolymer having larger hydrophobic polymer block tends to form an inverse structure. We find that the same is true for the $PEG350_7$-POSS-PS_n system. Increasing the molecular weight of the PS block would lead to the structural transition from polymer vesicles

to aggregated colloids when a series of hetero-arm block copolymers were allowed to self-assemble from acetone. Moreover, the self-assembled structure is also influenced by the architecture of block copolymer. The PEG350$_7$-POSS-(PS$_n$)$_2$ system can induce an inverse structure with a remarkably higher block ratio (f_{PEG} = 13.6%) than PEG350$_7$-POSS-PS$_n$ (f_{PEG} = 7.4 %).

The hydrophilic domain, PEG350$_7$-POSS, was prepared by introducing 7 PEG blocks onto a POSS cage, forming a highly branched hydrophilic building block. As a linker of block copolymers, POSS cage can generate more spatially branched hydrophilic structures than benzene does. Branched structure leads to an increased molecular area, based on our earlier studies, increased molecular area should be translated to a higher packing parameter (*P*), which means that inverse mesophases may be obtained with a higher block ratio, and it has been confirmed by our experimental results. Block copolymers PEG350$_7$-POSS-PS$_n$ would not tend to form inverse mesophases. The *f* values of PEG750$_3$-PS$_n$ have shown preferential self-assembly into inverse bicontinuous cubic mesophases in dioxane ranging from 5.4 to 5.7%, PEG350$_7$-POSS-(PS$_{509}$) (f_{PEG} = 4.6%) could still self-assemble into polymer vesicles, due to the declined value of packing parameter caused by an increased molecular area of hydrophilic block.

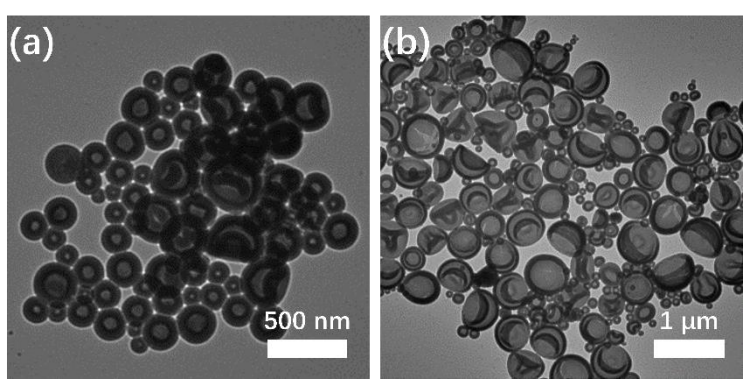


Figure 2.10. TEM images showing the polymer vesicles self-assembled by (a)

PEG_7-POSS-(PS_{442}) and (b) PEG_7-POSS-(PS_{509}) in dioxane.

Effect of the composition of the solvent on the morphology of hetero-arm block copolymer

The self-assembled structures of $PEG350_7$-POSS-$(PS_n)_2$ series, which have two PS chains, keep invariant no matter what solvent is used during our experiments. However, to the $PEG350_7$-POSS-PS_n system, Changing the composition of the organic solvent allows to form diverse morphologies of self-assembled structures, including polymer vesicles, polymer sponges, polymer cubosomes and aggregated colloids, in contrast to that all $PEG350_7$-POSS-PS_n hetero-arm block copolymers self-assemble into polymer vesicles in the dioxane-water system.

For examples, if the acetone was used as the organic solvent, the self-assembled structures of polymer $PEG350_7$-POSS-(PS_{211}) would not change obviously, $PEG350_7$-POSS-(PS_{259}) can generate an mixture of polymer vesicles and polymer sponges. As demonstrated above, $PEG350_7$-POSS-(PS_{317}) appears to form polymer cubosomes, more hydrophobic block copolymers $PEG350_7$-POSS-(PS_{442}) and $PEG350_7$-POSS-(PS_{509}) would form respectively polymer hexasomes and aggregated colloids. To clearly examine the effect of the composition of the solvent on the self-assembly of hetero-arm block copolymers, two of the most hydrophobic polymers have been used to self-assemble from the mixed solvent of acetone/dioxane with different mixing ratios. For the polymer $PEG350_7$-POSS-(PS_{442}), morphologies have successfully changed into polymer cubosomes when using the mixed solvent acetone/dioxane (v:v=90/10), and increasing the content of dioxane (20%) has lead

to the result in the formation of polymer vesicles. Under the same conditions, $PEG350_7$-POSS-(PS_{509}) can self-assemble into inversed micelles instead of aggregated colloids.

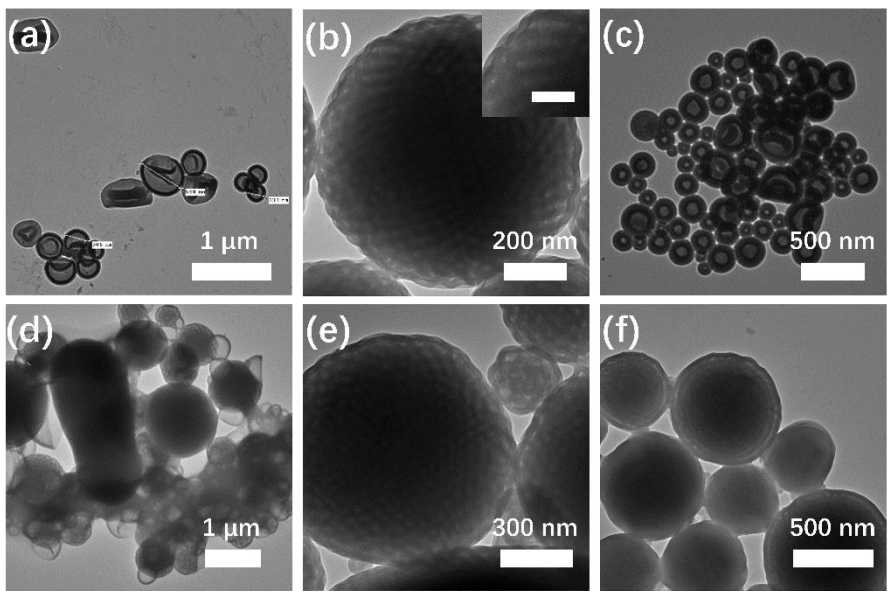


Figure 2.11. (a, b) TEM images showing the morphologies of PEG_7-POSS-(PS_{317}) self-assembled in (a) dioxane and (b) acetone; (c-f) TEM images showing the morphologies of PEG_7-POSS-(PS_{442}) self-assembled in (c) dioxane, (d) acetone/dioxane(v:v=80/20), (e) acetone/dioxane(v:v=90/10) and (f) acetone.

Above results strongly support that the composition of the solvent significantly influences the self-assembled structures of the hetero-arm block copolymers. Compared with the dioxane, the self-assembly of the hetero-arm block copolymers from acetone-water system was steered towards the formation of inverse mesophases.

3. Conclusion.

In this work, a series of POSS based hetero-arm block copolymers with different architectures and different molecular weights have been designed and synthesized. The self-assembly of both the PEG350$_7$-POSS-PS$_n$ and PEG350$_7$-POSS-(PS$_n$)$_2$ series demonstrates that the block ratios, the branched architectures, the POSS cage and the composition of solvents could be significant factors for the determination of the morphologies of self-assembled structures. In contrast to the conventional amphiphilic block copolymers, hetero-arm block copolymers based on a POSS cage do not tend to form inverse bicontinuous cubic mesophases by containing a much more branched hydrophilic domain. In particular, by changing the composition of the organic solvent, self-assembled behaviors of these systems may be totally changed. The apparent packing parameter could be remarkably increased by increasing the content of acetone. Our results could contribute to expanding the availability of highly defined periodic nanostructures created by solution self-assembly of block copolymers, which may have potential applications in the field of molecular separation and nanotemplating. Relevant studies are ongoing.

4. Experimental and Supporting Information

Materials.

POSS-octavinyl substituted (POSS) was purchased from Hwrkchemical and all other reagents were purchased from commercial sources and used as received unless otherwise noted. Dichloromethane (DCM) was dried (using CaH_2 under N_2 atmosphere) and distilled. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone under N_2 atmosphere and distilled before use. All reactions were performed in an inert atmosphere unless otherwise noted.

Characterization methods.

^{1}H NMR was recorded by Agilent 400-MR DD2 Magnetic Resonance System and Varian/Oxford As-500 using CD2Cl2 and CDCl3 as solvents and internal standards. Molecular weights and polydispersity indices of polymers and block copolymers were measured by Agilent 1260 Infinity gel permeation chromatography (GPC) system equipped with a PL gel 5μm MiniMIX-D column (Agilent Technologies) and differential refractive index detectors. THF was used as an eluent with a flow rate of 0.3 mL min^{-1} at 35 °C. A PS standard kit (Agilent Technologies) was used for calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectrometer (MALDI-TOF-MS) was performed on a Bruker Ultraflex II TOF-TOF mass spectrometer equipped with a nitrogenasler (335 nm). The analytical sample was prepared by mixing a THF solution of analyte with a THF solution of matrix.

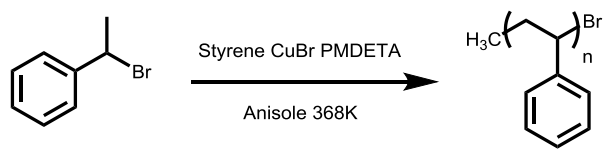
Scanning electron microscope (SEM) was performed on a Hitachi S-4300 at an acceleration voltage of 15 kV. The suspension was cast and dried on a slide glass, and coated with Pt by performed at a Malvern Zetasizer Nano-S. Transmission electron microscope (TEM) was performed on JEOL JEM-2100 microscope at 200 kV. Sample specimen were prepared by placing a drop of the sample solution on a carbon-coated Cu grid (200 mesh, EM Science). The grids were air-dried overnight.

Synchrotron Small Angle X-ray Scattering (SAXS) data were obtained on the 6D and 9A SAXS beam at Pohang acceleration laboratory in Korea (PLS-II, 3.0 GeV). The sample-to-detector distance (SDD) was 3.5 m and 6.5 m. respectively, the concentrated suspension of PCs was dried for 24 h in a freeze-dryer. Ti-SBA-15 was used as standard sample and scattering spectra of powder samples were taken in transmission mode at room temperature (11.6 keV).

Synthesis.

The hetero-arm block copolymers and important precursors were synthesized following the procedure shown as below.

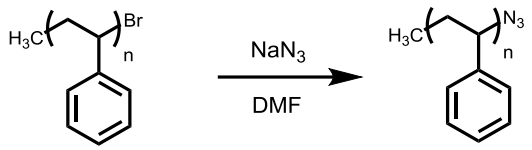
Synthesis of Brominated Polystyrene (**1**)



1

A 100 mL schlenk round bottom flask was charged with CuBr (8 eq.) in an inert atmosphere. Anisole (15% v/v_{Total}) and PMDETA (16 eq.) were added dropwise. After 15 min stirring, styrene (n eq.) and phenylethyl bromide (1 eq.) were added and the resulting solution was degassed for 20 min. Then the reaction was proceeded at 368 K and was quenched by exposing to the air and cooling down and diluted by dichloromethane. The solution was filtered through aluminum oxide eluted by dichloromethane to remove Cu catalyst, then most of solvent was evaporated and the crude product was precipitated into methanol. The white powder was dried under vacuum.

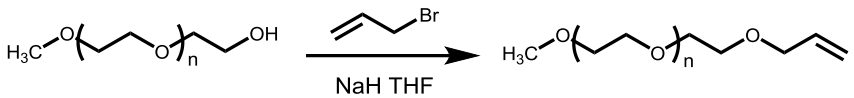
Synthesis of Azido-Functionalized Polystyrene (**2**)



1 **2**

Brominated polystyrene (**1**, 1 eq.) and NaN_3 (10 eq.) were dissolved in DMF under N_2 and stirred at room temperature. After 12 h, DMF was evaporated by a rotary evaporator, the residue was dissolved in DCM and washed by water and brine. The azido terminated polystyrene was precipitated into methanol and dried under vacuum.

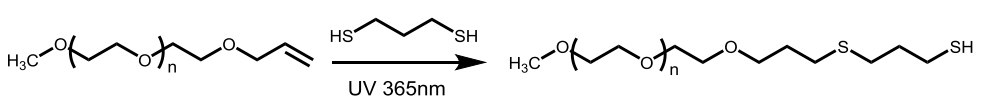
Synthesis of Vinyl Terminated Polyethylene Glycol (**3**)



3

A 250 mL schlenk round bottom flask was purged with dry N_2 and charged with NaH (1.2 g, 57.2 mmol), freshly distilled THF (100 mL) and cooled to 273 K. 50% solution of PEG mono methyl ether (Average Mw= 350, 10 g, 28.6 mmol) in THF was added via a syringe. The mixture was stirred for 1 h and then the 50% solution of allyl bromide (6.90 g, 57.2 mmol) in THF was added dropwise. Then after another 3 h reaction, 50 mL water was added to quench the reaction, the organic layer was separated out and dried by anhydrous Na_2SO_4 and then condensed to about 20 mL, 50 mL DCM was added to dissolve the remnant and washed with 50 mL water 3 times and then dried by anhydrous Na_2SO_4. After removing the solvent, the residue was transferred onto silica gel and eluted with DCM/Methanol (v/v=10:1) to obtain the product as yellow liquid (10.6 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.87 (m, 1H), 5.24 (t, 1H), 5.13 (d, 1H), 3.98 (d, 2H), 3.49-3.62 (m, 24-28 H), 3.33 (s, 3H).

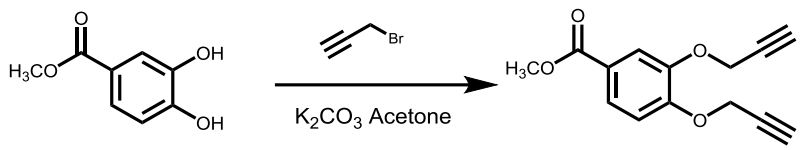
Synthesis of Thiol Terminated Polyethylene Glycol (**4**)



3 **4**

A 25 mL schlenk tube was purged with dry N_2 and charged with DMPA (60.0 mg, 0.234 mmol), vinyl terminated PEG (**3**, 5.00 g, 12.8 mmol) dissolved in 5 mL methanol and 1,3-dipropanedithiol (7.00 g, 64.8 mmol) were added dropwise, the reaction was complete after irradiation by 365 nm UV light for 2 h. Methanol was evaporated under a reduced pressure and the crude product was purified by column chromatography on a silica gel with DCM/Methanol (v/v=25:1) (4.9g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.52-3.66 (m, 24-28H), 3.37 (s, 3H), 2.61 (m, 6H), 1.86 (m, 4H), 1.36 (t, 1H).

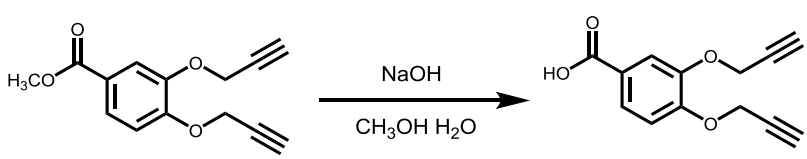
Synthesis of Methyl-3,4-dipropargyloxybenzoate (**5**)



5

In a 500 mL two necked round bottom flask, a mixture of Methyl-3,4-dihydroxylbenzonate (10.0 g, 59.0 mmol) and propargyl bromide (15.2 mL, 140 mmol) was dissolved in 200 mL acetone, then anhydrous K_2CO_3 (30 g) was added and the reaction was stirred for 24 h under reflux. Next, the solid was removed by filtration and the solvent was evaporated by a rotary evaporator. Water and DCM were added and the product was extracted to organic phase, The organic phase was separated and dried over anhydrous $MgSO_4$. The DCM was removed under a reduced pressure and the crude product was recrystallized in methanol to get compound **5** as yellow solid (69%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.72 (m, 2H), 7.06 (d, 1H), 4.81 (q, 4H), 3.89 (s, 3H), 2.54 (q, 2H).

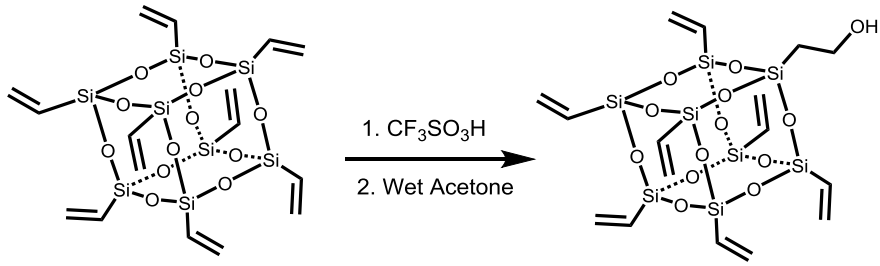
Synthesis of 3,4-dipropargyloxybenzoic acid (**6**)



5 **6**

Methyl-3,4-dipropargyloxybenzoate (**5**, 5.0 g, 22.4 mmol), was dissolved in 500 mL methanol, and aqueous NaOH (45 mL, wt. 10%, 100 mmol) was dropped via a syringe, the reaction was stirred for 72 h at room temperature and traced by TLC. The solvent was not removed until the reaction was completed. 2 M aqueous HCl was added to the mixture and the white solid was collected by vacuum filtration and dried under vacuum (83%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.79 (m, 2H), 7.11(d, 1H), 4.83 (q, 4H), 2.55 (q, 2H).

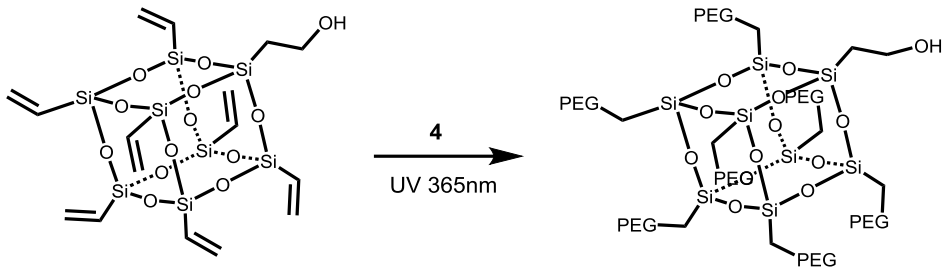
Synthesis of 3-hydroxylpropylheptavinyl-POSS (**7**)



7

Under an inert atmosphere, Trifluoromethanesulfonic acid (0,41 mL, 4.74 mmol) was slowly added dropwise via syringe to a solution of octavinyl-POSS (3.00 g, 4.74 mmol) in freshly distilled DCM (50 mL). After 4 hours reaction at room temperature, the mixture solution was firstly diluted by 40 mL DCM and then washed with 50 mL saturated aqueous NaHCO3 3 times, the organic phase was dried by anhydrous Na_2SO_4 and the solvent was removed under a reduced pressure. 30 mL DCM, 1 mL H_2O and 40 mL acetone were added into the remnant and the hydrolysis procedure was performed overnight, the crude product could be obtained by evaporating the solvent and purified by column chromatography on a silica gel with DCM/Hexane (v:v=3/1) to afford a white solid (28%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 5.88-6.16 (m, 21H), 3.84 (t, 2H), 1.17 (t, 2H).

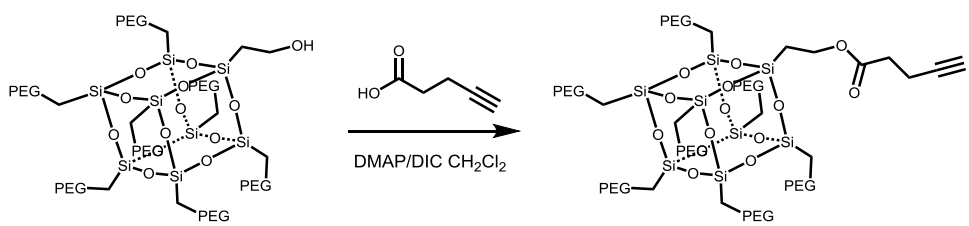
Synthesis of PEG350$_7$-3-hydroxylpropyl-POSS (**8**)



7 8

In a 25 mL schlenk tube equipped with a stirring bar, a mixture of 3-hydroxylpropylheptavinyl-POSS (**7**, 100 mg, 0.154 mmol) and DMPA (28.0 mg, 0.108 mmol) were dissolved in fleshly distilled THF (3.0 mL) under an inert atmosphere, thiol terminated polyethylene glycol (2.15 g, 4.31 mmol) dissolved in THF (3 mL) was added dropwise. The reaction was stirring at room temperature for 3 h under irradiation by 365 nm UV light. After removing the solvent, the thiol terminated polyethylene glycol was recollected by column chromatography on a silica gel with DCM/MeOH (v:v=30/1), by increasing the polarity to DCM/MeOH (v:v=10/1), the product was collected by subsequent elution (71%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.52-3.80 (m, 170-198H), 3.38 (s, 21H), 2.61 (m, 56H), 1.86 (p, 28H), 1.02 (t, 16H).

Synthesis of PEG350$_7$-3-(4'-pentyloxy)-propyl-POSS (**9a**)

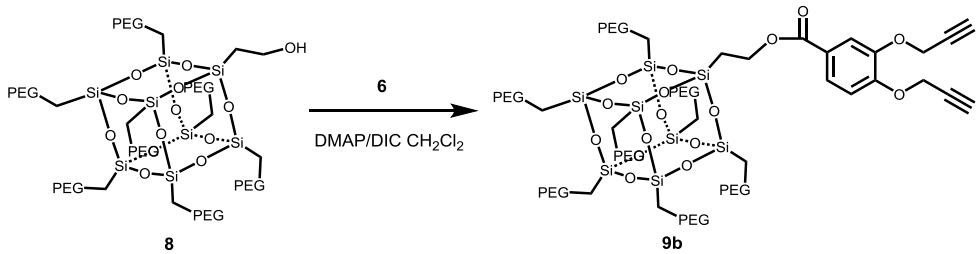


8 9a

To a 100 mL schlenk round bottom flask equipped with a stirring bar were added 4-pentynoic acid (147 mg, 1.50 mmol) and DMAP (61 mg, 0.50 mmol) in an inert atmosphere, the flask was cooled to 273 K, then DIC (227 mg, 1.80 mmol) and PEG350$_7$-3-hydroxylpropyl-POSS (**8**, 220 mg, 0.05 mmol) dissolved in freshly distilled DCM (10 mL) was added dropwise. After stirring for 10 min, the mixture was allowed to warm up to room temperature and stirred for 24h. Afterthat, precipitate was filtered off and the filtrate was washed with water and brine, dried

over anhydrous Na_2SO_4, and evaporated by a rotary evaporator. The residue was redissolved in DCM and purified by column chromatography. If necessary, preparatory size exclusion chromatography could be a subsequent method of purification (77%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 4.22 (t, 2H), 3.52-3.62 (m, 168-196H), 3.38 (s 21 H), 2.61 (m, 56H), 2.02 (t, 4H), 1.86 (p, 28H), 1.02 (t, 16H).

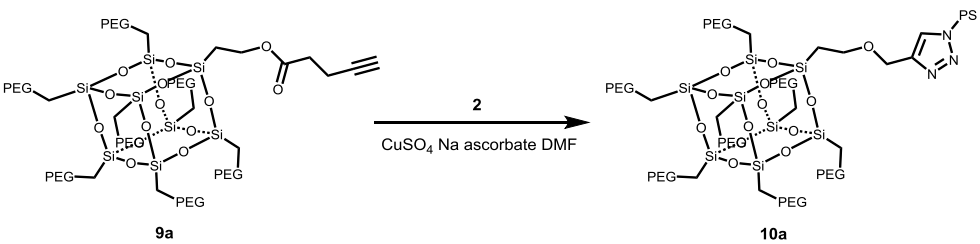
Synthesis of PEG350$_7$-3-(3',4'-dipropargyloxybenzoyloxy)-propyl-POSS (**10a**)



8 **9b**

Follow the same procedure as synthesis of PEG350$_7$-3-(4'-pentyloxy)-propyl-POSS (**9a**).

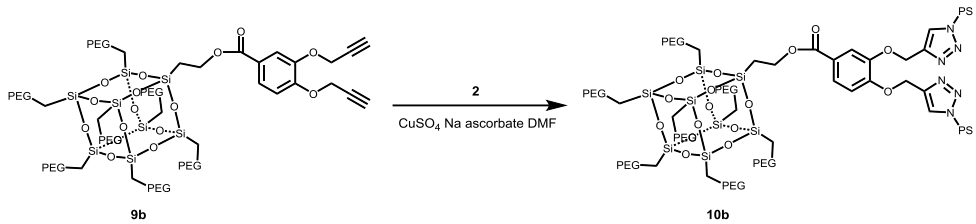
Synthesis of PEG350$_7$-POSS-PS (**9b**)



9a **10a**

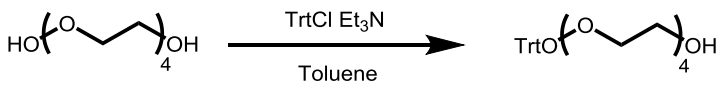
To a 100 mL schlenk round bottom flask equipped with a stirring bar were added azido terminated polystyrene (2 eq.), $CuSO_4 \cdot 5H_2O$ (6 eq.) and Na ascorbate (4 eq.) in an inert atmosphere, then PEG350$_7$-3-(4'-pentyloxy)-propyl-POSS (**9a**, 1eq.) dissolved in anhydrous DMF (10 mL) was added dropwise. The reaction was stirred at room temperature for 24 h. Next, DMF was removed by a rotary evaporator and the residue was redissolved in DCM and transferred onto a silica gel column, DCM was first used as a eluent to fully remove the unreacted polystyrene, then DCM/MeOH (v:v-=10/1) was used to wash the product off the column. After removing the solvent, the product was precipitated into methanol and dried under vacuum to afford a white powder (23%).

Synthesis of PEG350$_7$-POSS-PS$_2$ (**10b**)



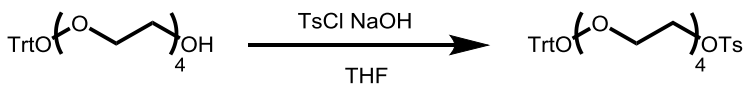
Follow the same procedure as Synthesis of PEG350$_7$-POSS-PS (**9b**).

Synthesis of Tetra(ethylene glycol) Trityl Ether.



To a 500 mL two-neck round bottom flask equipped with a stirring bar were added tetra(ethylene glycol) (50 mL, 6.4 eq.)‡ and toluene (50 mL), Azeotropic evaporation of residual water was performed on a rotary evaporator until ca. 35 mL of the liquid was collected. The side neck was equipped with a glass hose barb adapter connected to an N_2 line and triethylamine (8 mL, 1.3 eq.) was added in one portion by using a syringe under stirring. Trityl chloride (12.5 g, 1 eq.) was added through a glass funnel through the main neck against the N2 gas flow. After 3 h of stirring at room temperature, the mixture was diluted with ethyl acetate (50 mL) and then the mixture was filtered and the The filtrate was transferred to a 500 mL separation funnel and washed with water, saturated aqueous solution of ammonium chloride and brine, dried over anhydrous Na_2SO_4. And the solvent was removed evaporated by a rotary evaporator.

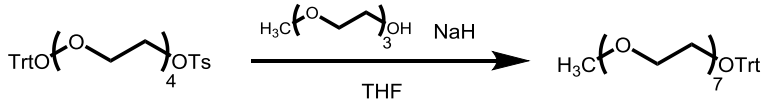
Synthesis of Tetra(ethylene glycol) Trityl Tther p-Toluenesulfonate.



Tetra(ethylene glycol) trityl ether put into a 500 mL round-bottomed flask equipped with an magnetic stir bar was dissolved in THF (60 mL). The mixture was stirred

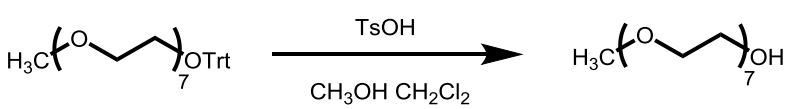
and cooled for 30 minutes on a water-ice bath. Sodium hydroxide (6.25 g, 4 eq.) was dissolved in distilled water (20 mL) and was added through a glass funnel. p-Toluenesulfonyl chloride (8.5 g, 1.14 eq.) dissolved in THF (40 mL) was added slowly to the stirred reaction mixture over 15 min. The mixture was stirred at 0 °C for 5 h and then the ice bath was removed and the mixture was stirred at room temperature overnight. Then the reaction mixture was diluted with water (30 mL) and ether (50 mL) and transferred to a separating funnel. The aqueous layer was discarded and the organic layer is washed with water and brine. The mixture was dried over anhydrous Na_2SO_4 and the solvent was removed evaporated by a rotary evaporator.

Synthesis of Hepta(ethylene glycol) Methyl Trityl Ether.



A 500 mL schlenk round bottom flask was purged with dry N_2 and charged with NaH (1.87 g, 1.8 eq.), freshly distilled THF (100 mL) and cooled to 273 K. 50% solution of tri(ethylene glycol) mono methyl ether (5.0 g, 1.2 eq.) in THF was added via a syringe. The mixture was stirred for 1 h and then the 50% solution of tetra(ethylene glycol) trityl ether p-toluenesulfonate (15.0 g, 1.0 eq.) in THF was added dropwise. Then after another 3 h reaction, 50 mL water was added to quench the reaction, the organic layer was separated out and dried by anhydrous Na_2SO_4 and then condensed to about 20 mL, 50 mL DCM was added to dissolve the remnant and washed with 50 mL water 3 times and then dried by anhydrous Na_2SO_4. After removing the solvent, the residue was transferred onto silica gel and eluted with DCM/Methanol (v/v=10:1) to obtain the product as yellow liquid (10.1 g, 68 %).

Synthesis of Hepta(ethylene glycol) Mono Methyl Ether.



A 500 mL round bottom flask was purged with dry N_2 and charged with hepta(ethylene glycol) methyl trityl ether (10.1 g, 1.0 eq.), p-toluenesulfonic acid

(0.60 g, 0.2 eq.). 50 mL DCM and 50 mL methanol were added through a syringe. The mixture was stirred at room temperature overnight and then the solvent was removed under a reduced pressure. The remnant was transferred onto silica gel and eluted with DCM/Methanol (v/v=10:1) to obtain the product as colorless liquid (4.9 g, 83 %).

Synthesis of Vinyl Terminated Hepta(polyethylene glycol)

Follow the same procedure as Synthesis of Vinyl Terminated Polyethylene Glycol (**3**).

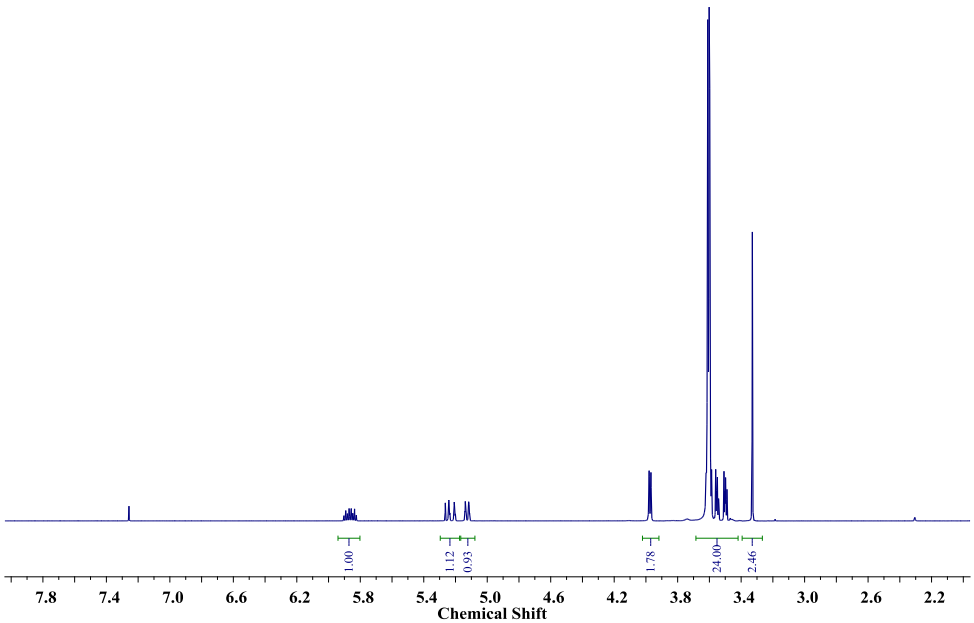
Synthesis of Thiol Terminated Hepta(polyethylene glycol)

Follow the same procedure as Synthesis of Thiol Terminated Polyethylene Glycol (**4**).

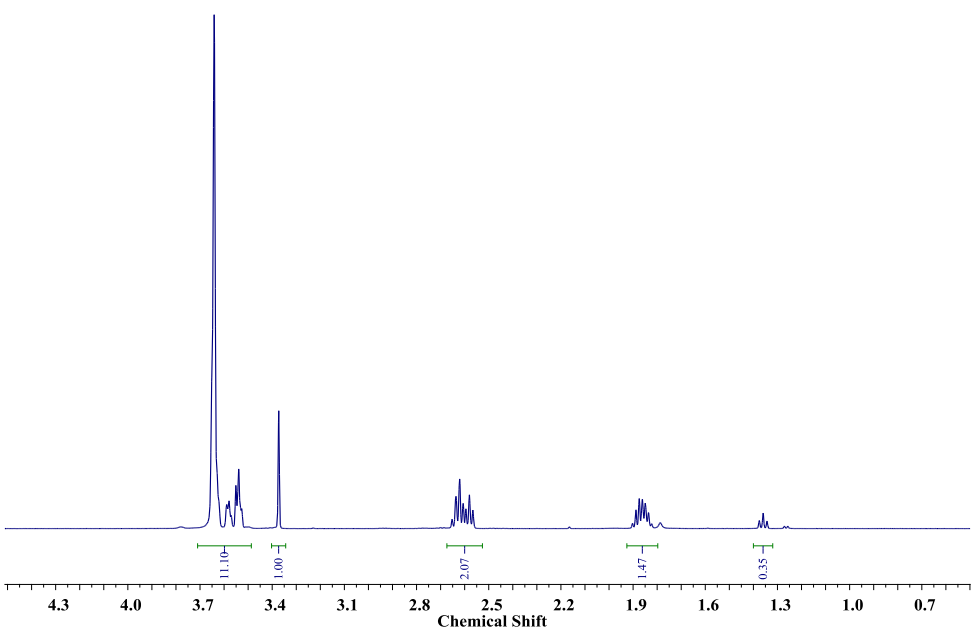
Synthesis of hepta-PEG_7-3-hydroxylpropyl-POSS

Follow the same procedure as Synthesis of $PEG350_7$-3-hydroxylpropyl-POSS (**6**).

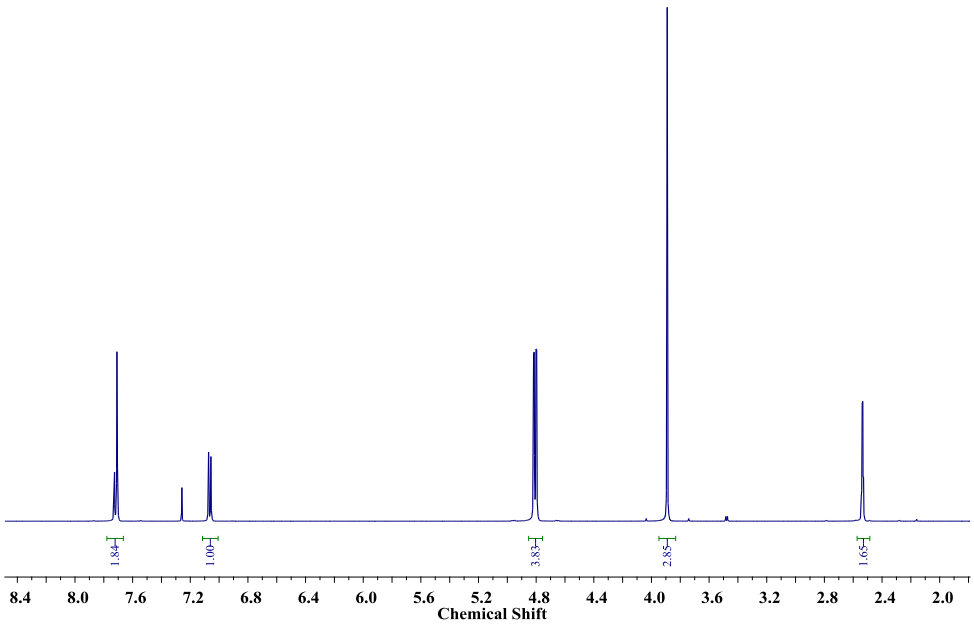
Supporting information (Spectra)



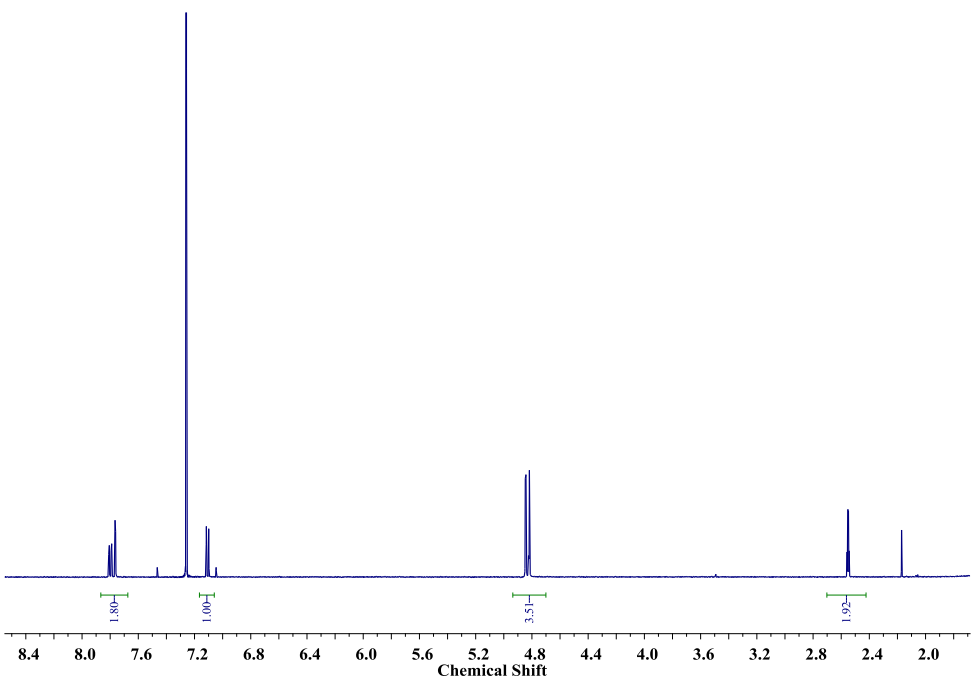
^{1}H NMR data of Vinyl Terminated Polyethylene Glycol (Compound **3**)



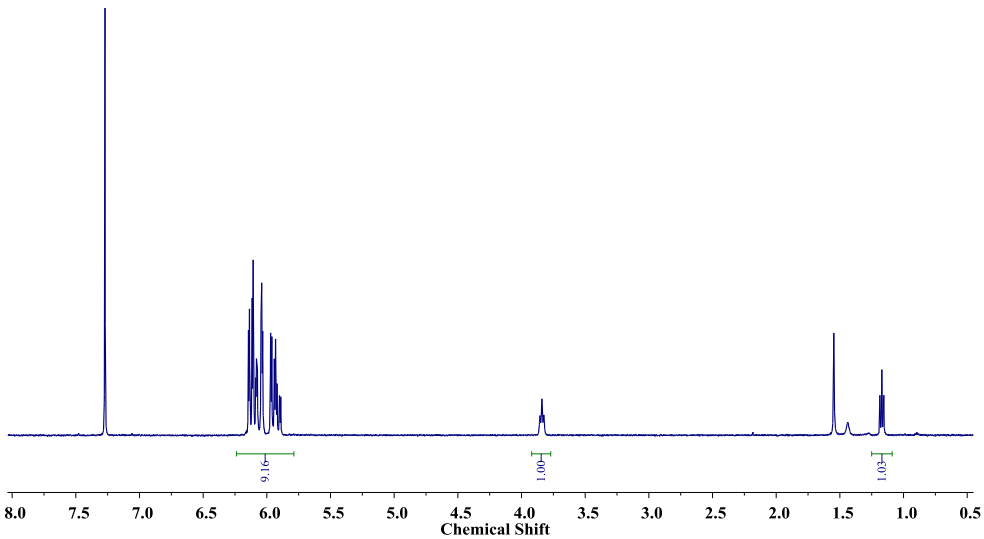
^{1}H NMR data of Thiol Terminated Polyethylene Glycol (Compound **4**)



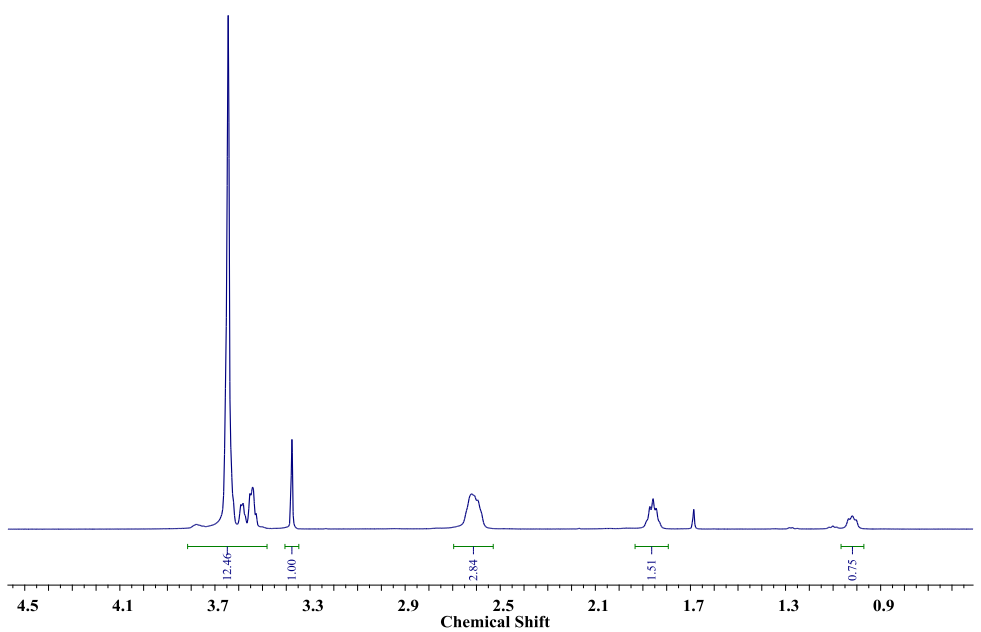
^{1}H NMR data of Methyl-3,4-dipropargyloxybenzoate (Compound **5**)



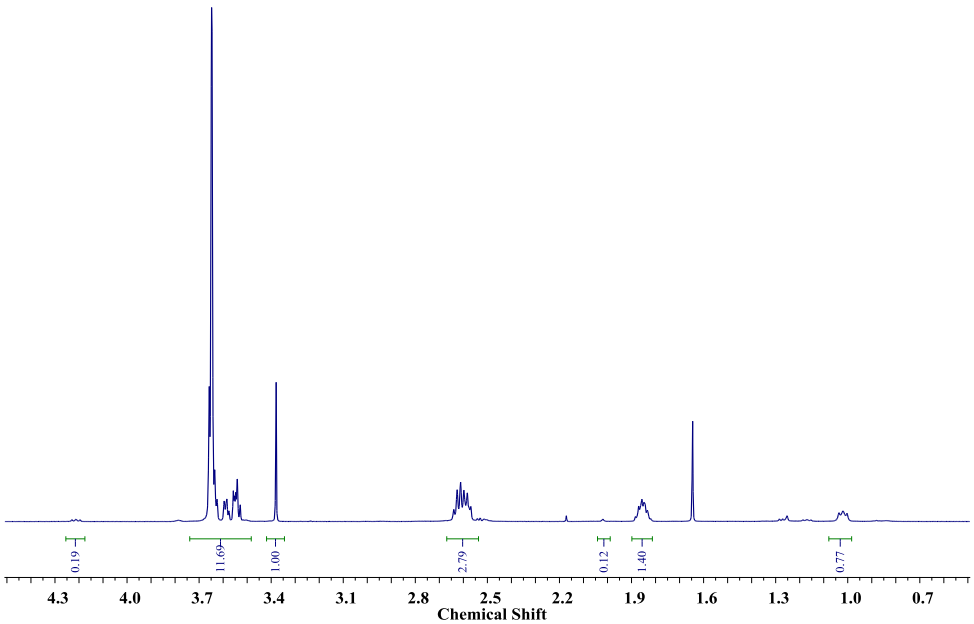
^{1}H NMR data of 3,4-dipropargyloxybenzoic acid (Compound **6**)



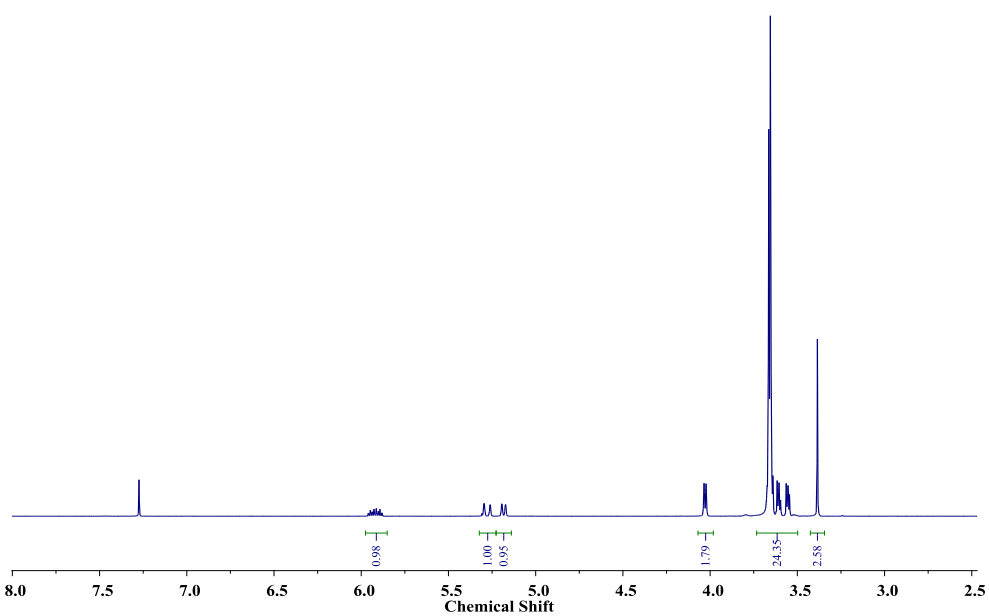
^{1}H NMR data of 3-hydroxylpropylheptavinyl-POSS (Compound **7**)



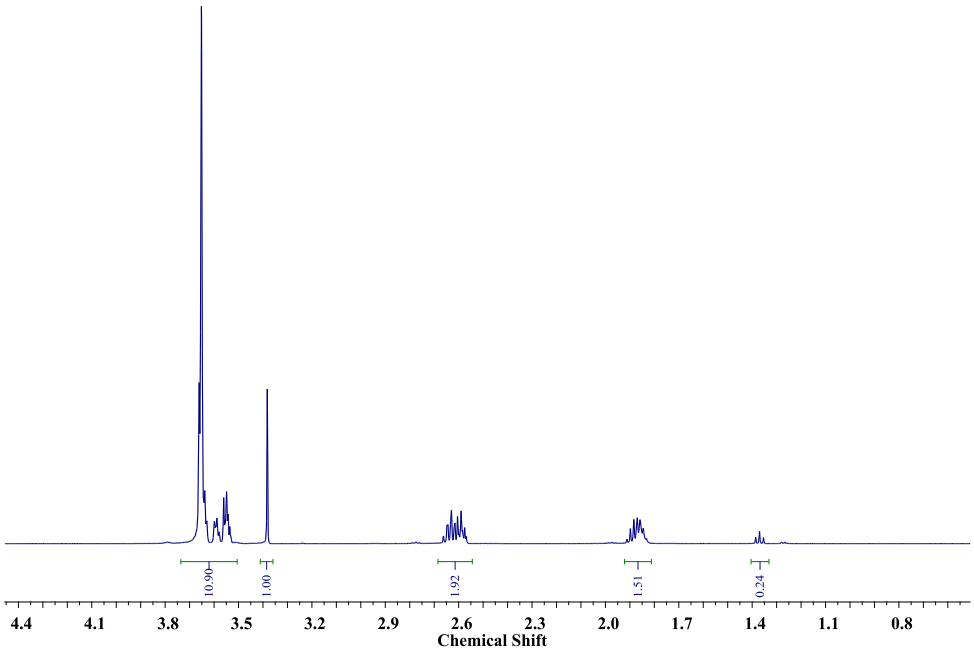
^{1}H NMR data of PEG350$_{7}$-3-hydroxylpropyl-POSS (Compound **8**)



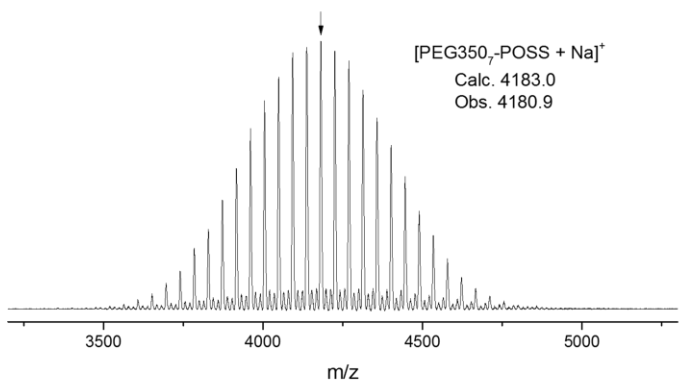
^{1}H NMR data of PEG350$_{7}$-3-(4'-pentyloxy)-propyl-POSS (Compound **9a**)



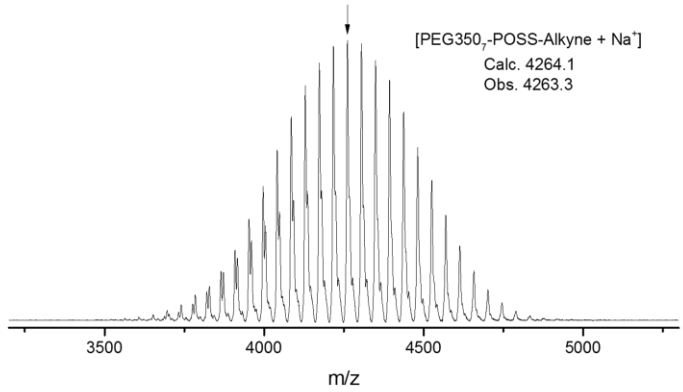
^{1}H NMR data of Hepta(ethylene glycol) Mono Methyl Ether.



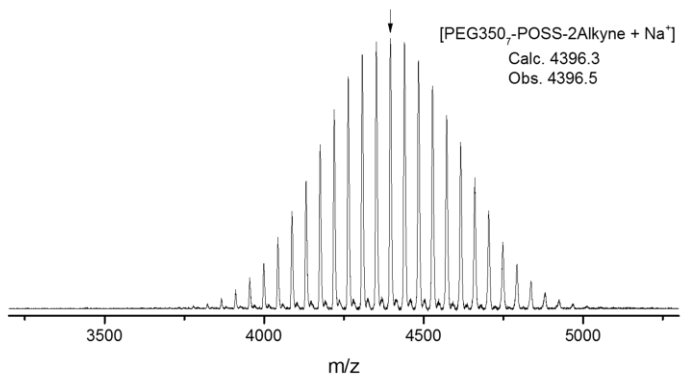
^{1}H NMR data of Thiol Terminated Hepta(polyethylene glycol)



MALDI-TOF-MS spectra of PEG350$_7$-3-hydroxylpropyl-POSS (Compound **8**)



MALDI-TOF-MS spectra of PEG350$_7$-3-(4'-pentyloxy)-propyl-POSS (Compound **9a**)



MALDI-TOF-MS spectra of PEG350$_7$-3-(3',4'-dipropargyloxybenzoyloxy)-propyl-POSS (Compound **10a**)

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국문 초록

포스를 기반으로 한 블록 공중합체의 합성 및 용액 자기조립 연구

Sun Yulin

화학부 고분자화학 전공

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블록 공중합체는 수용액 상에 자기 조립을 통하여 고분자 입방결정 구조가 형성되는 것이 재미있는 현상이다. 형상되는 고분자 입방결정 구조가 안쪽에 워터 채널이 존재하는 3 차원적인 다공재료로 이용할 수 있다. 고분자의 아키텍처 구조가 자기 조립에 영향을 미칠 수 있는데, 본 연구에 정육면체 구조를 가지는 케이지 본자인 포스(POSS)를 이용하여 케이지의 코너에서 폴리에틸렌글라이콜(PEG) 블록과 폴리스타이렌(PS)를 정확하게 도입 시키어 새로온 아키텍처 구조를 가지는 블록 공종합체를 합성하였다. 블록 공중합체의 분자량, 화학적인 구조 그리고 용매를 조절하면서 수용액 자기 조립 실험을 진행하여 보았다. 결론적으로 고분자 재료로 쓰일 수 있는 고분자 입방결정을 얻었고, 포스 케이지가 수용액 자기 조립에 미치는 영향을 분석하였다.

주요어: Hetero-Arm 폴리머, 포스, 폴리에틸렌글라이콜,
폴리스타이렌, 수용액 상 자기조립, 나노 구조.

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